Crystallographic Orientation of a Palladium-defect Pair in Germanium from Perturbed Angular Correlation Spectroscopy

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Time differential perturbed angular correlation spectroscopy was performed for different orientations of crystalline germanium following diluted doping of the material with the hyperfine interactions probe ^{100}Pd/^{100}Rh. Results are interpreted in order to identify the crystallographic orientation of a palladium-defect pairing that is most pronounced following annealing at 500 °C. Orientation in the <100> direction can be excluded. The data are consistent with a substitutional palladium atom pairing with a vacancy in a nearest-neighbours configuration and the pair being oriented in the <111> direction. This is similar to the palladium-vacancy pairing known to occur in n-type silicon.

1. Introduction

Palladium (Pd) has been shown to induce Metal Induced Crystallisation (MIC) of germanium at a lower temperature than many other metals, such as, for example, Cu, Ni, Co or Pt [1-3]. Following MIC, Pd atoms may be left behind in crystalline Ge. Consequently the performance of devices based on this material may be affected. With time differential perturbed angular correlation (TDPAC) spectroscopy using the probe ^{100}Pd/^{100}Rh, the local lattice environment of palladium point defects can be studied.

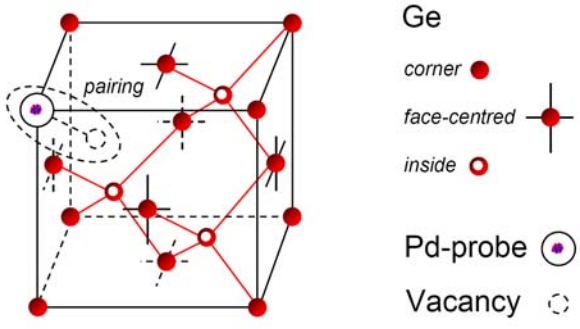

Fig. 1. Illustration of a Pd-vacancy pair in the diamond lattice of germanium oriented in the <111> direction.

Previous TDPAC measurements with the ^{100}Pd/^{100}Rh probe on intrinsic germanium identified a non-zero electric field gradient (EFG) at the probe location [4, 5]. The EFG may be caused by the pairing of a Pd-atom with a neighbouring defect, most likely a vacancy. This is illustrated in Fig. 1 for a <111> orientation.

It has been shown [5] that the defect pairing is most pronounced after annealing the germanium at 500 °C. Further annealing at 700 °C dissociates the pair. The measured quadrupole coupling constant ν_Q associated with the observed EFG is close to that which has been observed for ^{100}Pd/^{100}Rh in highly doped n-type silicon by Dogra *et al.*

[6-10]. This may suggest that both effects are of similar origin. In silicon the effect has been attributed to the formation of Pd-vacancy pairs, with the Pd being substitutional and the vacancy located in the <111> crystallographic direction. This directionality has been inferred from TDPAC orientation measurements [9, 10]. Equivalent orientation measurements for ^{100}Pd/^{100}Rh in intrinsic germanium were outstanding and have now been performed. Initial results are presented and discussed in this paper.

2. Experimental Details

The ^{100}Pd/^{100}Rh probe nuclei were synthesized with the 14 UD Pelletron accelerator at the Australian National University in Canberra via the fusion evaporation reaction ^{92}Zr(^{12}C, 4n)^{100}Pd [11]. The ^{12}C beam energy was 70 MeV. Synthesized probe nuclei were recoil-implanted with energies of several MeV into a germanium specimen cleaved from a (100) germanium wafer. Cleaving occurred on (110) planes.

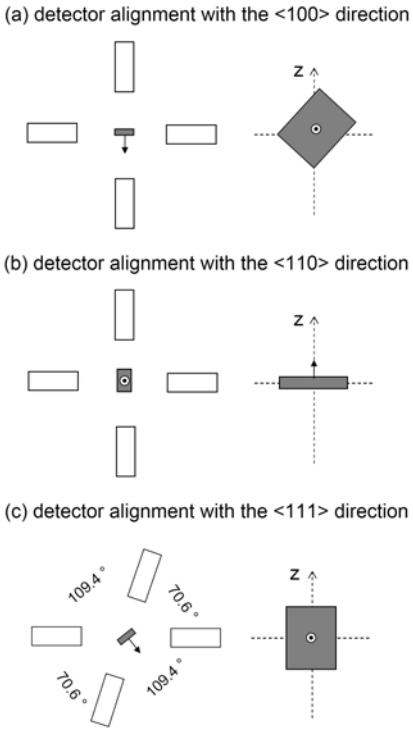

Fig. 2. Respective orientations of the detector array and the germanium specimen (grey). The arrow points in the <100> direction.

The as-implanted germanium specimen was annealed for 20 min at 500 °C in argon flow inside a tube furnace. The TDPAC spectroscopy [12, 13] was performed using a conventional set-up of four cylindrical NaI scintillation detectors forming a planar array. Detectors provided both start and stop signals to a time-to-analogue converter (TAC). The coincidence time distributions of the two γ-rays in the 84 keV - 74 keV $\gamma - \gamma$ cascade in ^{100}Rh were recorded for all detector combinations using NIM-standard electronics [4]. These two γ-rays populate and depopulate the intermediate 2^+ state in ^{100}Rh.

Three measurements were performed with detectors aligned with the <100>, the <110> and the <111> crystallographic directions, respectively. This is illustrated in Figure 2. All time distributions obtained were corrected for statistical background events. The distributions for the 90° (70.6°) detector combinations and those for the 180° (109.4°) detector combinations were averaged, thus compensating for differences in detection solid angle and detector efficiency. Finally, using the conventional prescription, the ratio function *R(t)* was extracted from the data [12].

A modulation of *R(t)* may be associated with a precession of the γ - γ anisotropy about the direction of the EFG [12,13]. Varying the respective orientation of detector axes and EFG direction modifies the modulation of the ratio function. The comparison of ratio functions *R(t)* measured for different specimen orientations therefore permits the determination of the crystallographic direction of the electric field gradient.

3. Results and Discussion

Figure 3 shows the ratio functions *R(t)* measured for the three specimen orientations. The data consistently show at t = 110 ns the first minimum of the modulation pattern observed previously [4, 5] with an associated quadrupole coupling constant of ν_Q = 10.6 (2) MHz. However, in contrast to the previous measurements, the modulation is less pronounced. The fraction of ^{100}Pd probe atoms pairing with the defect is thus smaller. The local maximum expected near t = 220 ns is only barely visible. This is due to damping of the ratio function caused by non-unique probe environments. It is likely that the annealing procedure applied in the present work either insufficiently cured implantation-induced lattice modifications or, alternatively, has led to the dissociation of Pd-defect pairs, which was previously observed following annealing at 700 °C.

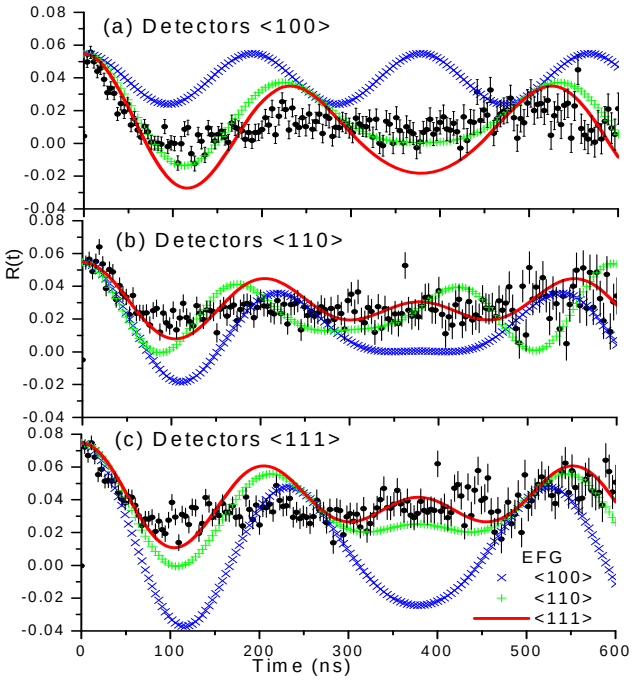

Fig. 3. Measured ratio functions *R(t)* for ^{100}Pd/^{100}Rh in germanium for the three specimen orientations. Calculations assuming that every palladium probe atom pairs with a vacancy in an otherwise undisturbed lattice are shown for the EFG orientations <100>, <110> and <111>.

It may tentatively be observed that for detector alignment with the <100> direction (Fig. 3a) a modulation exists with two possible maxima near t = 220 ns and 500 ns, which are separated by a broad minimum between 300 ns and 400 ns. Figs 3b and c show that detector alignment with the <110> and <111> axes results in a larger mean value of *R(t)* than apparent in Fig. 3a for alignment with the <100> direction. Also, a local maximum between t = 300 ns and 400 ns may exist for both of these two specimen orientations.

Ratio functions can be simulated and fitted using the code *Nightmare* which is based on the routine *NNFit* [14]. Such simulations are also displayed in Figure 3 for all three specimen orientations studied. The calculations assume defect pair alignment, and thus EFG direction, either along a <100> direction, or a <110> direction or a <111> direction, respectively. The simulations further assumed no deviation from axial symmetry (η = 0), a single 100% probe fraction representing the Pd-vacancy pair and a unique local lattice environment excluding damping. The simulations for EFG direction along a <111> axis correspond to the orientation of the defect pair that is illustrated in Fig. 1.

The calculations show that different respective orientations of detector axes and EFG direction result in different modulation patterns in the corresponding ratio function. In particular, the mean of the ratio function varies. Furthermore, depending on detection geometry, a local extremum near t = 370 ns is either pronounced or somewhat attenuated. Careful inspection of the modulation patterns of *R(t)* suggests that the defect pair is either oriented, as expected, in the crystallographic <111> direction, or possibly in the <110> direction.

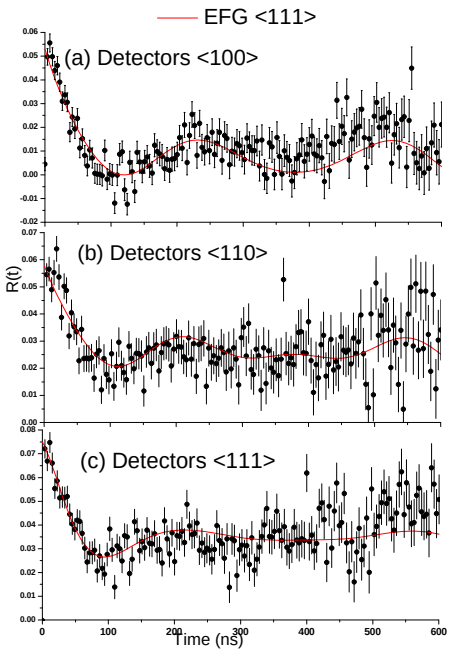

Fig. 4. Measured ratio functions *R(t)* for ^{100}Pd/^{100}Rh in germanium for the three specimen orientations. The data are compared with a calculation that assumes that about 25% of the palladium probe atoms pair with vacancies and that the defect pair and EFG are oriented in the <111> direction.

Figure 4 compares the data with more detailed *Nightmare* calculations that assume defect pair orientation in a crystallographic <111> direction. Agreement is good for an assumed probe fraction of 25% pairing with the defect in an otherwise undisturbed lattice environment and the remainder of probes having diverse non-unique lattice environments.

4. Summary and Conclusions

Time differential perturbed angular correlation spectroscopy was performed for different orientations of a germanium specimen that had been recoil-implanted with the hyperfine interactions probe ^{100}Pd/^{100}Rh. The results confirm the quadrupole coupling constant associated with a palladium-vacancy pairing that had been discovered previously. The probe fraction forming this defect-pair in the present specimen was, however, smaller. Tentative interpretation of the data excludes orientation along the <100> direction. Instead the data are consistent with a palladium-defect dumbbell that is oriented in the expected <111> direction. Improved annealing of the sample following probe implantation in future work may strengthen this interpretation.

References

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